J Mater Cycles Waste Manag
DOI 10.1007/s10163-015-0418-3

ORIGINAL ARTICLE

Leaching characteristics of the fine fraction from an excavated landfill: physico-chemical characterization

Fabio Kaczala[1] · Mohammad Hadi Mehdinejad[2] · Allar Lääne[3] · Kaja Orupõld[3] · Amit Bhatnagar[4] · Mait Kriipsalu[5] · William Hogland[1]

Received: 10 February 2015 / Accepted: 3 July 2015

Abstract Leaching of fine fraction (<10 mm) obtained from landfill mining activities in an Estonian landfill was done. On-site excavation was carried out in four test pits (TP_1, TP_2, TP_3, TP_4) that were further divided in four layers (L_1, L_2, L_3, L_4). Total chemical oxygen demand (COD_t), dissolved chemical oxygen demand (COD_d), total organic carbon (TOC), dissolved organic carbon (DOC) and metals (Zn, Cu, Pb and Cd) were analyzed. The results showed that approximately 70 % of COD_t were in particulate/colloidal state. The TOC released ranged between 2326 and 3530-mg/kg dry matter for test pits suggesting spatial differences in the studied landfill. DOC ranged between 365–874 and 317–940 mg/kg for different test pits and sampling layers, respectively. Low average leaching rates of metals were observed (0.2–1.5 %). Pb had a significantly higher average leaching rate (1.0 %) compared to Zn (0.70 %) and Cu (0.35 %). The potential use of COD_t as a surrogate indicator of TOC, DOC and Zn on the basis of high correlation coefficients was observed. To conclude, the implementation of adequate strategies to manage fine-grained fractions obtained from excavated waste relies on physico-chemical characterization of both the fine fractions itself and the leachate generated during storage and use.

Keywords Landfill mining · Leachate · Heavy metals · TOC · DOC

✉ Fabio Kaczala
fabio.kaczala@lnu.se

[1] Department of Biology and Environmental Sciences, Faculty of Health and Life Sciences, School of Natural Sciences, Linnaeus University, LNU, Landgången 3, SE-391 82 Kalmar, Sweden

[2] Environmental Health Research Center, Faculty of Health, Golestan University of Medical Sciences, Gorgan, Iran

[3] Estonian University of Life Sciences, Institute of Agricultural and Environmental Sciences, Tartu, Estonia

[4] Department of Environmental Sciences, University of Eastern Finland, Kuopio, Finland

[5] Department of Water Management, Estonian University of Life Sciences, Institute of Forestry and Rural Engineering, Tartu, Estonia

Introduction

Landfilling has been one of the most dominant ways of solid waste disposal in many parts of the world [1, 2] due to relatively low initial investments and operational costs [3]. Countries such as the USA and Australia are largely dependent on landfilling, whereas Germany, Sweden, Denmark, The Netherlands and Austria had less than 5 % of their municipal solid wastes landfilled in the year of 2008 [1]. Even though landfill implementation has been practiced worldwide, there is a clear decreasing trend in recent years and the thousands of landfills in operation nowadays will likely be closed in the next 10–30 years [1]. Moreover, apart from landfills in use, there are thousands of landfills all over the world that have been either abandoned or closed. Hogland [4] has reported the existence of between 75,000 and 100,000 closed or abandoned landfill/dump sites in the Baltic Sea Region, Northern Europe. In China, about 1000 landfills were closed due to environmental concerns in the last decade [3]. Landfills pose enormous risks to human health and the environment as a consequence of gaseous emissions of volatile organic compounds, methane, carbon dioxide, airborne particulate matter [5] and also the generation of leachate causing serious constraints in water recipients, soil and the atmosphere [6]. Despite the closure of landfills, threats for the

Published online: 17 July 2015

environment and human health still remain for a long period [7].

However, a contradiction in relation to landfills is that as environmental and human health concerns have been constantly raised, landfills can also be viewed as a secondary source of materials (plastics, glass and metals) and energy (direct collection of methane or energy recovery through incineration of materials with high calorific values such as plastics). At the same time, global demand for raw materials has tremendously increased in the past few decades resulting in both higher costs and increased environmental impacts during extraction, processing and use [8]. Furthermore, high concerns have been raised in relation to long-term availability of natural resources [9] and metals such as copper and iron are likely to be depleted in the near future. Therefore, there is a need for the implementation of new models of resource management that combine the current challenges of high demands and overexploitation of natural resources and materials scarcity and environmental problems caused by landfills. According to Krook and Baas [9], the society needs to consider that previously extracted and used resources are not permanently lost and can be re-extracted from waste deposits such as landfills, slag heaps and tailing ponds. Landfill excavation/mining with the objectives of recyclables recovery combined with remediation, creates new volumes in existing landfills and creates space for new infrastructure [8] such as parks, jogging tracks and leisure areas. As stated by Krook and Baas [9], landfill mining initiatives taking place in the 1980s and 90s were mainly addressed to solve landfill management issues such as lack of landfill void space, local pollution concerns and interference with urban expansion. However, nowadays, the main motivation for landfill mining can be the possibilities of resource recovery, and as the main focus has shifted towards material and energy recovery, it is of crucial importance to have a detailed knowledge of both waste composition of the landfill and further treatability/processing and destination in early stages of the project implementation.

Several studies have addressed waste characterization primarily by screening the waste into different particle sizes followed by manual sorting into different waste categories [4, 8, 10, 11]. One of the main findings obtained from waste characterization has been reported by Hogland [4], which states that fine fraction (<18 mm) can contribute to more than 50 % of the total mass of an excavated landfill. High contents of fine fraction in excavated waste have also been recently reported by Masi et al. [2] with approximately 70 % of the total waste excavated from a closed dumpsite in Southern Italy being <10 mm. According to Kaartinen et al. [8], the fine fraction has been considered a potential substrate for intermediate or final cover layers of landfills in operation or for closed and excavated landfills, which can be a revenue source [4]. However, even though the fine fraction is an important contributor to the total mass of an excavated landfill, the composition of fine fraction and also the potential environmental and ecological disturbances are rarely studied and reported in the literature. The leaching and release of chemical constituents from the fine fraction upon contact with rain water during storage and also in the case this is used as cover material of excavated/mined landfills can result in potential risks to the environment. According to Mahmoudkhani et al. [12], the first step to propose an adequate strategy for the fine fractions obtained from excavated landfills is to identify in laboratory scale leaching properties of the material in question. Leaching tests can bring valuable information regarding the compliance with existing standards established for different purposes. Furthermore, excavated waste must be stored before it reaches the final destination and the knowledge of leaching properties brings also basic information on how to design and implement proper storage areas and stormwater/leachate treatment on the basis of potential environmental and ecological impacts. Therefore, the current research carried out a general characterization of the leachate generated by the fine fraction (<10 mm) of a full-scale excavated landfill located in Kudjape, Saarema Island, in Estonia. The characterization was based on classical physico-chemical parameters such as chemical oxygen demand (COD) in soluble and particulate form, total organic carbon (TOC), dissolved organic carbon (DOC) and metal contents, since these parameters are widely used as proxy indicators of potential environmental and ecological problems and are widely established in most of the existing environmental quality standards and guidelines. Furthermore, it is important to highlight that knowledge of such proxy indicators brings also valuable insights in terms of leachate treatment design and implementation. The sampling procedure was designed in order to verify the hypothesis that whereas (1) physico-chemical characteristics of leachate from fine fraction have no significant variation over different locations in the landfill (spatial variation), (2) physico-chemical characteristics of leachate originated from fine fraction sampled from different layers (temporal variation) are significantly different. Although the leachate was produced artificially in laboratory scale, the goal of this study is to use the obtained knowledge as preliminary information for the potential use of such material in the future.

Materials and methods

Description of the landfill site

The fine fraction (<10 mm) was obtained from landfill mining activities that took place at Kudjape Landfill, located in the Island of Saaremaa (N 58:16:06, E 22:32:23), 2 km southeast from Kuressaare town, Estonia during February 2013. The dumping area consisted of two sections: (1) the old section with an approximate 1.2 ha that received an estimated volume of 35,000 m^3 between 1970 and 2000 and, (2) the new section with an approximate 2.7 ha with an approximate volume of 158,000 m^3 of disposed waste which was received between 2000 and 2009. The landfill received mainly municipal solid wastes. The composition of the waste disposed in the landfill in the excavated section during the years 2007 and 2008 is shown in the Table 1.

The waste was initially disposed on a flat unlined area 4 m above the sea level and it reached a final height of approximately 12 m by the landfill closure. A compactor was used to prepare the area for new incoming waste during the last 10 years, and no intermediate cover layers existed. A thin layer of gravel was covering a flat area of the landfill since 2009. Average annual temperature at the site is 5.6 °C and annual precipitation is 594 mm.

Sampling procedures

The sampling at Kudjape Landfill was done in the new section of the landfill that had an approximate area of 2.7 ha and received wastes from 2000 to 2009. The sampling was carried out by a tread excavator machine (Volvo EC210B 21 tonnes) with an attached bucket of 1 m^3 excavation capacity. Four test pits (TP_1, TP_2, TP_3, TP_4) spatially distributed over the flat top landfill area, which were then divided in four sampling depths (L_1, L_2, L_3, L_4), were excavated. The main goal of excavating different test pits divided into different sampling depths was to evaluate how the leachate from the excavated waste varied in terms of spatial distribution within the landfill and also temporally considering the deeper sampling layer within a test pit, the older the waste. The approximate aging at the time of excavations for each layer was: L_1 (4–5 years), L_2 (5–6 years), L_3 (6–7 years), L_4 (7–8 years). The fine fraction was later used to build a methane degradation cover. Each test pit had a total excavation depth of approximately 5 m including the 30–50 cm topsoil cover layer that was previously removed; thus, each layer had an approximate depth of 1 m, and sample volume of 1 m^3. An example of one test pit and respective sampling layers is illustrated in Fig. 1.

As soon as 1 m^3 of waste was excavated from each layer within a specific test pit, the waste was fed into a trommel screen Doppstadt SM518 for an initial separation of the waste in two fractions: (1) >40 mm and (2) <40 mm. The fraction <40 mm was further screened down to <10 mm which was the fraction (fine-grained fraction) used for the leaching tests reported in this study. Considering four test pits with samples taken in four different layers, a total of 16 samples of fine fraction, approximately 10 L each, were transported to the laboratory and stored under 4 °C until the leaching tests were performed.

Table 1 The mass in tons of different types of waste disposed in the studied landfill during 2007 and 2008

Type of waste	2007	2008
Mixed municipal waste	8122	6863
Construction and demolition waste	690	456
Plastic waste	49	111
Food waste from meat and fish industry	195	203
Asbestos roofing and pipes	117	80
Hospital and veterinary waste	4	1
Screenings from wastewater treatment plant	87	23
Clothes	7	11
Textile	2	7
Street sweepings	8	1
Bulky waste, furniture, carpets	17	29
Ash	3	6

Fig. 1 Excavation of test pit 1 (TP_1) with excavation layers indicated with *red lines*

Sample preparation for the leaching tests

Leaching tests were done with eight composite sub-samples obtained from the 16 original ones (four test pits with four different layers each) in order to evaluate the spatial variability and the influence of waste age on leaching properties. Composite sub-samples from the test pits (TP_X) and the different sampling layers (L_X) were obtained as follows (Eqs. 1 and 2):

$$TP_X = L_{1X} + L_{2X} + L_{3X} + L_{4X} \quad (1)$$

$$L_X = TP_{1X} + TP_{2X} + TP_{3X} + TP_{4X} \quad (2)$$

where X is the number of the test pit (1–4) and the layers (1–4), respectively.

Leaching test

The batch-leaching tests were carried out according to the Swedish Standard Method SS-EN 12457-2 with minor modifications. The SS-EN 12457-2 recommends the use of particle size of <4 mm; however, since the main objective of this investigation was to study the leaching properties of the fine fraction as close as possible to the real conditions the investigation was done with particle size <10 mm. The liquid/solid ratio (L/S) of 10 L/kg was achieved using deionized water.

In order to consider the moisture content of the fine fraction the amount of dried waste (kg dry matter) and deionized water to achieve the proposed liquid/solid ratio was calculated according to the Eq. 3 as follows:

$$L_{10} = (10 - MC/100) \times M_d \quad (3)$$

where MC is the moisture content of the fine fraction (%); M_d is the dry mass of the fine fraction (kg dry matter) and L_{10} is the amount of water needed to achieve the L/S of 10-L/kg dry matter.

Leaching tests were carried out in a flocculator/jar test (STUART-SW6) for 24 h under agitation speed of 100 rpm in 800 mL beakers at ambient temperature (23 ± 1 °C). After 24 h agitation, the fine fraction settled down for 30 min and samples from the supernatant phase (eluent) were taken for further physico-chemical characterization. Eluents were stored in 50 mL falcon tubes at 4 °C for total organic carbon (TOC), dissolved organic carbon (DOC), total chemical oxygen demand (COD_t), dissolved chemical oxygen demand (COD_d) and metal analysis (Zn, Cu, Cd and Pb). Falcon tubes that received eluents for metal analysis were previously acid-washed (0.1 M nitric acid). Electrical conductivity (EC) (mS/cm), pH and oxidation–reduction potential (ORP) were measured during the leaching tests in pre-determined intervals to avoid any influence of chemical transformations. All leaching tests were performed in triplicates.

Analytical procedures

Physico-chemical characterization of the leachate was done for: COD_t, COD_d, TOC, DOC and the metals zinc (Zn), copper (Cu), lead (Pb) and cadmium (Cd). Prior to the analysis of COD_d and DOC, samples were filtered through a GF/C Whatman filter 1.2 µm (Cat No 1822-047). All parameters with the exception of metals were analyzed with Dr. Lange cuvette tests (Dr. Bruno Lange, GmbH & CO. KG, Dusseldorf, Germany) and measured spectrophotometrically with a HACH XION 500 spectrophotometer (DR 5000 HACH). All Lange methods are validated according to ISO 8466-1 [13], DIN 32645 [14] and DIN 38402 A51 [15].

The metals Zn, Cu, Pb and Cd in leachates were analyzed after filtration through 0.45 µm filters attached to 50 mL syringes by atomic absorption spectroscopy—AAS (Model Analyst 4). Analysis of Cd was performed using atomic absorption spectrophotometer (AA-6800, Shimadzu) equipped with graphite furnace atomizer (GFA-EX7). The Quantification of the selected metals in the fine fraction (solid phase) was performed with a portable Olympus DELTA DS-4000 Handheld X-ray Analyzer (Olympus).

Statistical analysis

Descriptive statistics such as minimum and maximum, mean and standard deviation values were calculated for all the physico-chemical parameters. Pearson's correlation coefficients (non-parametric) were calculated to evaluate possible associations between leachate quality constituents since the correlation analysis between chemical constituents has been reported as a useful statistical tool to identify quality parameters that might serve as surrogates for others [16]. However, for practical purposes only correlation coefficients higher than 0.6 have been considered for surrogates in this study. The comparison between test pits and layers was carried out through one-way ANOVA followed by Tukey's multiple comparison tests. All the statistical analyses were performed by the statistical software GraphPad Prism (version 5.02 for Windows, GraphPad Software Inc., San Diego, USA) assuming Gaussian distribution and variance homogeneity at a significance level of $p \leq 0.05$.

Results and discussion

3.1 pH

The Fig. 2 shows the variation of pH during 24 h of leaching in the different test pits and respective sampling

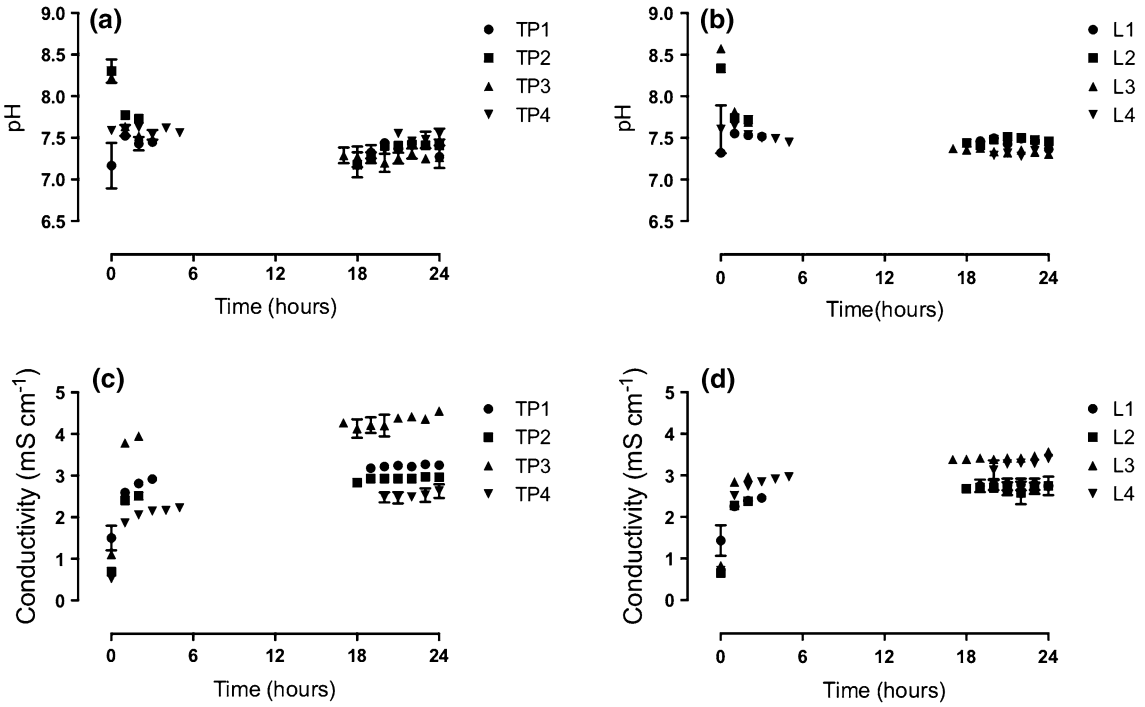

Fig. 2 pH and conductivity dynamics during 24 h of leaching test, ($n = 3$)

layers. The results have shown that leachate generated from different test pits had their pHs ranging between 7.1 and 8.3 corresponding to a coefficient of variation of less than 5 %. The highest initial pHs were observed in TP_2 and TP_3, respectively. Although the leachate from TP_1 slightly increased from 7.1 up to 7.5 during the test, leachates from TP_2, TP_3 and TP_4 had pHs reduced from 8.3, 8.2 and 7.6 down to 7.1, 7.2, and 7.35, respectively. According to one-way ANOVA test, pHs from test pits were not significantly different ($p < 0.05$). Leachates extracted from the different sampling layers had pH values in similar ranges of those observed for test pits (Fig. 2), and whereas pHs from L_1 (upper layer) and L_4 (bottom layer) had a negligible decrease throughout the leaching test, middle layers (L_2 and L_3) had their initial pHs of 8.4 and 8.6 decreased down to 7.3 and 7.2, respectively, after 24 h (Fig. 2). According to Slomczyńska and Slomczyński [17], leachates with pHs in the range of those found in this current study—slightly alkaline and alkaline—are related to landfills with solid wastes disposed for more than 5 years and that already have achieved a complete methanogenic phase.

Electrical conductivity and oxidation–reduction potential

The dynamics of conductivity throughout the leaching test is presented in Fig. 2 which shows that conductivity in the initial stage of the experiment (0 h) ranged between 0.5–1.5 and 0.65–1.4 mS/cm and at the end (24 h) between 2.7–4.6 and 2.75–3.6 mS/cm for test pits and different sampling layers, respectively. The results have shown an increase in conductivity during the first 4–5 h followed by an equilibrium state suggesting that an increase in ionic strength and changes in pH take place simultaneously until the equilibrium state is achieved (Fig. 2) although no correlation between pH and conductivity was found. According to a one-way ANOVA Tukey's test ($p < 0.05$), the leachate of test pit 3 (4.6 mS/cm) had a significantly higher conductivity in comparison to the others. On the other hand, no statistical differences were observed between conductivities of leachates generated by different sampling layers, although deeper layers (L_3 and L_4) had their conductivities after 24 h as high as 3.4 and 3.6 mS/cm, respectively (Fig. 2). Redox potential was measured only in the beginning of the experiment (0 h) and in the end (24 h) and the results obtained have shown a wider range of values in the initial stage of the experiment in comparison to the end. The initial values ranged between 147–224 and 144–201 mV for different test pits and layers, respectively, whereas in the end narrower ranges were observed (209–220 mV for test pits and 203–216 mV for different layers).

Total chemical oxygen demand (COD_t) and dissolved chemical oxygen demand (COD_d)

The total chemical oxygen demand (COD_t) and dissolved chemical oxygen demand (COD_d) from the different test pits and sampling layers are presented in Fig. 3. The COD_t of the leachate extracted in all test pits was significantly different ($p < 0.05$) and ranged between 4924 and 7622 mg/kg (Fig. 3a). TP_4 and TP_3 were the ones with the lowest and the highest amounts of COD_t released per unit mass of dry fine fraction, respectively. The COD_t released from the different layers was also significantly different ($p < 0.05$), and whereas the highest COD_t was observed in the deeper layers with 7543 and 5520 mg/kg released by L_3 and L_4, respectively (Fig. 3b), upper layers (L_1 and L_2) released COD_t values as low as 3623 and 3572 mg/kg ($p > 0.05$). According to Ziyang et al. [18], the knowledge of the different fractions of COD is an important pre-requisite for the selection of proper leachate treatment in landfills and as observed in this study, most of the COD fraction released into the water was in particulate/colloidal state. The Fig. 3 illustrates the amounts of COD_d released into the solution and values ranging between 651 and 1904 mg/kg for test pits and 455 and 1561 mg/kg for different sampling layers (Fig. 3a). The amounts of COD_d corresponded to 28, 14, 16 and 13 % of the COD_t in TP_1, TP_2, TP_3 and TP_4, respectively (Fig. 3a). The highest contribution of dissolved matter was observed in the leachate of TP_1 (28 %) and this might be related to the specific environmental conditions of the excavated area. Oxygen diffusion is a factor that enhances the hydrolysis and the transformation of suspended macromolecular substances into lower molecular weight matters [18], which might have caused the current observation.

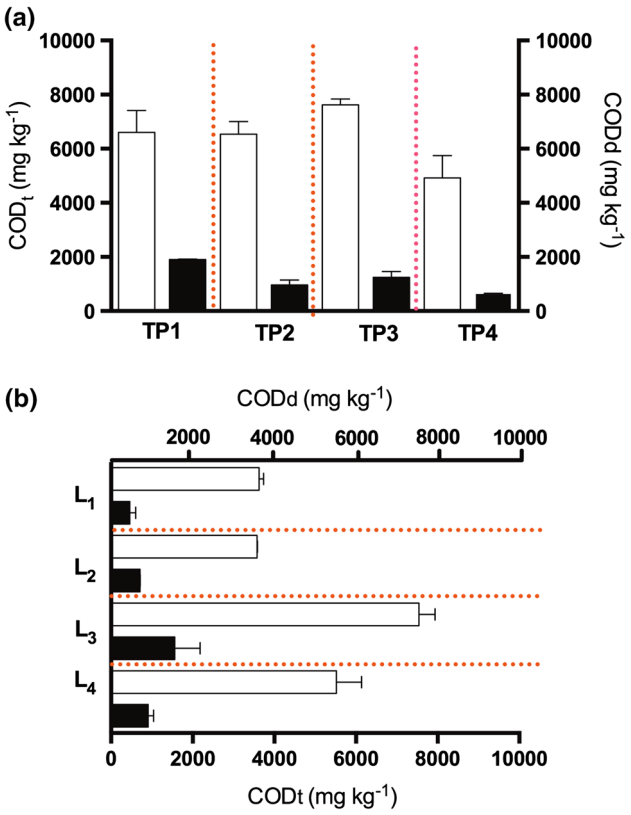

Fig. 3 COD_t and COD_d leached per unit mass of waste (mg kg^{-1}) in samples taken from the different test pits and layers, ($n = 3$)

Considering the amount of COD_d in comparison of COD_t, values as low as those observed for test pits were observed in the leachate of the different sampling layers with corresponding values of COD_d ranging between 12 and 20 % of COD_t (Fig. 3b). The low contribution of only 12 % in the upper layer (L_1) might be due to the relatively young age of the excavated waste (approximately 10 years old waste) with short time for hydrolysis to take place. However, it is important to emphasize that the types of waste discarded in a landfill do not solely determine the leachate composition and existing conditions in the waste body such as chemical and biological transformations and also interactions of contaminants with plant-derived matter need to be considered [5].

Total organic carbon and dissolved organic carbon

The results obtained for TOC and DOC released into the water phase from different test pits and layers during the leaching of 24 h are shown in the Fig. 4. There was a significant difference observed in TOC between all test pits ($p < 0.05$) with TP_3 releasing significantly higher amounts of TOC (3530 mg/kg dry matter) in comparison to TP_1 (2519 mg/kg dry matter) and TP_4 (2326 mg/kg dry matter) suggesting different stages of biodegradation processes spatially distributed within the excavated landfill. Considering the layers, as illustrated in Fig. 4b, values as high as 3069 and 2470 mg/kg of TOC were observed for L_3 and L_4, respectively, in comparison to values as low as 1894 and 1999 mg/kg for upper and intermediate layers (L_1 and L_2).

Dissolved organic matter was evaluated as DOC and concentrations ranging between 365–874 and 317–940 mg/kg for different test pits (Fig. 4a) and sampling layers (Fig. 4b), respectively, were observed. The highest leaching of DOC was observed for TP_1 and L_3 with concentrations as high as 874 and 940 mg/kg, being significantly higher than the others ($p < 0.05$).

Regarding the results observed for L_3, high TOC values combined with the contribution of 30 % of DOC (Fig. 4b) suggest transportation of fine fraction responsible for the presence of dissolved organic matter from upper layers downwards deeper areas of the landfill and consequent fine fraction built up with slower rates of degradation due to lack of optimum environmental conditions. According to Slack et al. [5], bio-decomposition of putrescible wastes is

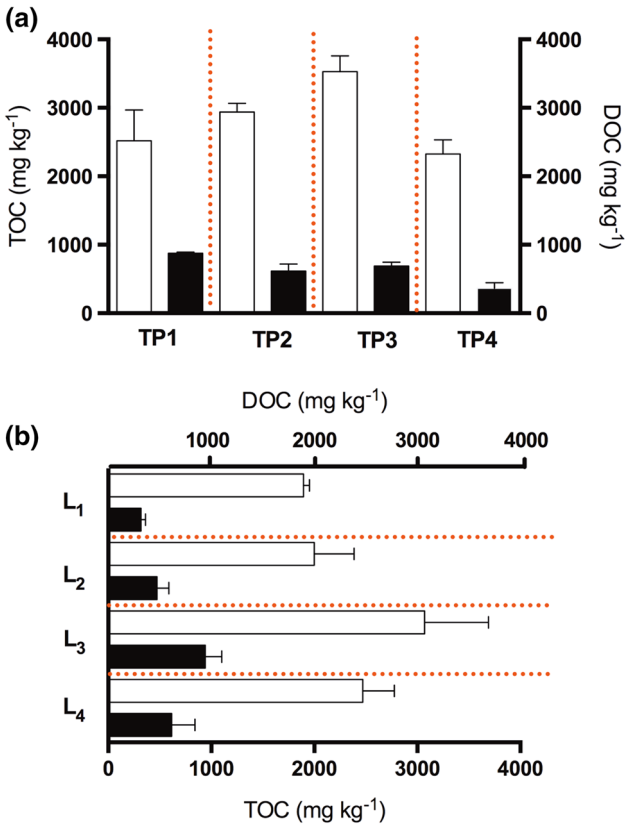

Fig. 4 TOC and DOC leached per unit mass of waste (mg kg^{-1}) in samples taken from the different layers and test pits, ($n = 3$)

responsible for an increase in the amounts of DOC in leachate suggesting transportation of such putrescible matter downwards.

Considering TP_1, the low TOC observed might be related to a higher rate of hydrolysis and further degradation, a fact that is corroborated by 38 % of the total carbon content being in hydrolyzed phase (Fig. 4a). This highlights that even though material composition within a specific landfill does not vary, environmental and physical conditions such as oxygen diffusion, moisture content, void space and waste compactness can play important roles in the leachate generated and concentrations of carbon contents in particulate and dissolved forms. However, it is important to emphasize that dynamics of organic matter transformation and mineralization in landfills is relatively complex and highly dependent on the environmental conditions [6] and whether chemistry or biology controls the solubility of organic matter and how different factors interact is not well known yet and further investigation is required.

Metals

The total concentrations of Zn, Pb, Cu and Cd released into the aqueous phase from different samples are presented in the Fig. 5. The amounts of Zn, Pb and Cu released by unit mass in different test pits ranged between 3.19–6.85, 0.90–1.35 and 0.13–0.40 mg/kg, respectively, whereas released Cd was as low as 1.00–3.00 µg/kg. A comparison of the metals released by the different test pits has shown that metals were significantly different among them (One-way ANOVA $p < 0.05$) and considering TP_3, a statistically higher amount of Zn was released in comparison to the others. Furthermore, the amounts of Cu released were significantly different ($p < 0.05$) in the following order: $TP_4 < TP_3 < TP_2 < TP_1$ (Fig. 5e).

Considering the layers, whereas Zn was released in higher amounts with values ranging between 2.65 and 6.30 mg/kg (Fig. 5b), Cd was released in concentrations ranging between 2.00 and 3.00 µg/kg (Fig. 5h). Intermediate concentrations were observed for Pb and Cu with released amounts per unit dry mass as low as 1.00–1.30 and 0.15–0.18 mg/kg, respectively (Fig. 5d, f). Although the obtained results did not show any well-defined pattern in relation to upper and deeper layers Zn, Pb, Cu and Cd were significantly different when comparing the different sampling layers (One-way ANOVA, $p < 0.05$). By analyzing the results based only on concentration released into the aqueous phase one can either overestimate or underestimate the mobility of certain chemical constituents into the water and potential environmental impacts. Therefore, leaching rates (%) of each metal were calculated on the basis of the concentrations found in the solid phase and actual concentrations detected on the artificial leachate (Table 2). According to Table 2, very low average leaching rates (%) ranging between 0.2 and 1.5 % were observed which might be explained by the lower solubility of these metals in alkaline pHs resulting in negligible concentrations in the artificial leachate. Since Cd concentrations in the fine fraction were under the detection limit of XRF equipment used, the leaching rates of Cd are not presented in Table 2. However, the leaching rate of Cd was possible to estimate based on the results of Cd analysis with ICP (data not shown) where Cd concentration approximately 1 mg/kg in the fine fraction was obtained. Thus, based on those results leaching rates for Cd would reach a maximum of 0.26 %.

Low leaching rates of Cu, Zn and Pb as observed in this study are comparable to previous investigation carried out by [19]. Even though Zn had the highest amounts released into the water, Pb had the highest leaching rate (%) suggesting lower affinity with the fine fraction and higher mobility (Fig. 6). According to a One-way ANOVA test, Pb had an average leaching rate of 1.0 % which was significantly higher in comparison to Zn (0.70 %) and Cu (0.35 %) suggesting that total concentrations of metals in the solid phase do not correspond to the amounts leached into the water and the potential mobility (Table 2). The partition process between solid phase and the solution can be highly influenced by a variety of geochemical aspects

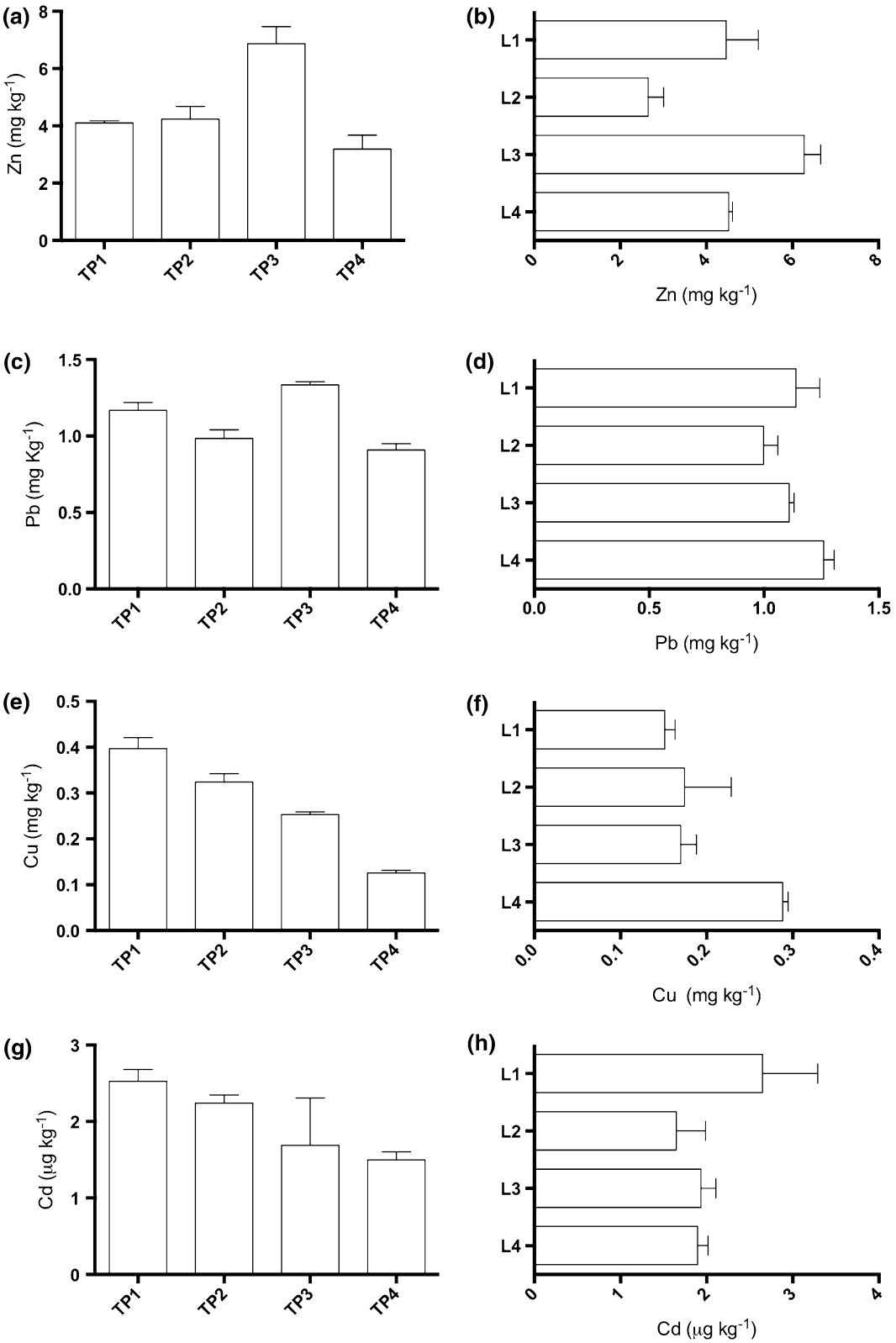

Fig. 5 The amounts of metals Zn, Pb, Cu (mg kg^{-1}) and Cd (µg kg^{-1}) leached per unit mass of waste in samples taken from the different test pits and layers, ($n = 3$)

Table 2 The concentration of studied metals in the solid matrix, aqueous phase and respective leaching rates (%) of studied metals in different locations (test pits) and layers of the excavated landfill

Sample	Cu (mg kg^{-1})			Zn (mg kg^{-1})			Pb (mg kg^{-1})		
	Solid phase	Leached	Leaching rate (%)	Solid phase	Leached	Leaching rate (%)	Solid phase	Leached	Leaching rate (%)
TP_1	105.2	0.4	0.4	845.3	4.1	0.5	119.2	1.2	1.0
TP_2	86.3	0.3	0.4	680.2	4.2	0.6	88.5	1.0	1.1
TP_3	45.3	0.3	0.6	732.8	6.9	0.9	147.0	1.3	0.9
TP_4	53.4	0.1	0.2	469.0	3.2	0.7	88.3	0.9	1.0
L_1	69.5	0.2	0.2	904.7	4.5	0.5	129.0	1.1	0.9
L_2	95.4	0.2	0.2	429.8	2.6	0.6	67.3	1.0	1.5
L_3	44.5	0.2	0.4	1068.5	6.3	0.6	134.5	1.1	0.8
L_4	58.8	0.3	0.5	436.2	4.5	1.0	108.0	1.3	1.2

Leaching rate (%) = (concentration liquid phase × 100)/(concentration solid matrix)

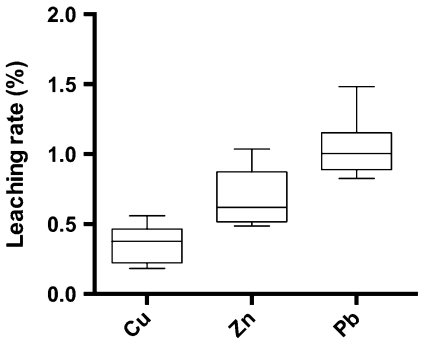

Fig. 6 *Box*-and-*whisker plots* showing minimum, average, maximum, lower quartile (25 %) and upper quartile (75 %) values of obtained leaching rates (%) of the studied metals, ($n = 8$)

such as pH, mineral weathering, transport by DOC, precipitation/dissolution mechanisms, adsorption/desorption processes and others [20] which makes it difficult to draw robust conclusions regarding which could have been the main factor that caused a significant higher leaching rate (%) of Pb in comparison to Zn and Cu in the current study. Low leaching rates (%) of metals as observed in this study have been highlighted by Slack et al. [5] and the reported leaching rates of disposed metals in landfills within the first 30 years were as low as ≤0.02 % due to metal immobilization by organic/inorganic sorption and precipitation.

Correlation analysis between water quality parameters

The possibilities of identifying surrogate indicators among all water constituents were evaluated and Pearson correlation coefficients were calculated with a 95 % confidence level. Table 3 shows the obtained correlation coefficients (r) and confidence values (p values) above and below the diagonal, respectively. The results have shown very good

Table 3 Pearson correlation coefficients (r value, above the diagonal line) and probability values (p values, below the diagonal line) between characteristics indicators

	Zn	Pb	Cu	Cd	DOC	TOC	COD_t	COD_d
Zn		**0.71**	0.10	0.13	0.57	0.81	0.77	0.46
Pb	**0.05**		0.38	0.44	0.40	0.43	0.42	0.37
Cu	0.81	0.36		0.44	0.55	0.33	0.48	0.63
Cd	0.76	0.27	0.28		0.21	−0.20	−0.06	0.30
DOC	0.14	0.33	0.15	0.61		**0.65**	**0.83**	**0.95**
TOC	**0.01**	0.28	0.43	0.63	0.08		**0.94**	0.57
COD_t	**0.03**	0.30	0.23	0.89	**0.01**	**0.00**		**0.78**
COD_d	0.25	0.36	0.09	0.47	**0.00**	0.14	**0.02**	

High correlation coefficients and probability values <0.05 are shown in bold

correlation between COD_t and both TOC and DOC with observed correlation coefficients as high as 0.94 and 0.83, respectively ($p < 0.05$). Such high and significant correlations suggest the potential use of COD_t as a surrogate indicator of organic carbon in both suspended and dissolved forms. Furthermore, COD_t was also highly correlated with COD_d ($r = 0.78$, $p < 0.05$) and Zn ($r = 0.77$, $p < 0.05$). Correlation of Zn with COD_t might be a result of either Zn-based organic complexes or metal chlorides. The interaction of Zn with organic carbon is confirmed with correlation coefficients as high as $r = 0.81$, $p < 0.05$ (Table 3). Whereas Pb has shown to be significantly correlated with Zn ($r = 0.71$, $p < 0.05$), no further correlation was observed with the other studied water quality parameters. Previous correlation analysis in the literature [16] and the results described above indicate that such statistical tests can be a useful tool in monitoring programs whose fine fractions of excavated landfills are used as soil cover after reclamation and area recovery. As soon as appropriate mathematical relationships are established, a shorter list of

water quality parameters may serve as a substitute for a larger list, bringing advantages as regards: (1) considerable reductions in analytical costs and time during a characterization and monitoring study, (2) the use of surrogates to plan and design a treatment system, and (3) the use of surrogates to evaluate the performance of treatment systems with reduced costs. However, it is important to mention that transferability of statistical relationships of leachate from fine fractions (<10 mm) of different landfills is a complex process that needs further evaluation.

Conclusions

The characteristics of the artificial leachate of the fine fraction (<10 mm) from an excavated landfill located in the city of Kudjape, Saarema Island, in Estonia were investigated. The results have shown that leachate from the different test pits and layers did not follow a well-defined pattern. The results suggest the existence of different biodegradation stages in different parts of the excavated landfill even though the composition of disposed waste had no major differences confirming the complex environmental and physical conditions in landfills. Regarding contaminants release from fine fraction, the results suggest that most of it can be found in particulate matter suggesting that physical methods such as settling/sedimentation and/or filtration can be potential ways of tackling leachate generated from fines when stored outdoors during landfill excavations. Furthermore, an evaluation of actual leaching rates (%) in relation to metals may be a much more useful tool than concentrations found in solid phase since it was observed considerably low leaching rates suggesting that regardless the concentration, metals release occur according to different environmental conditions existing in the landfill such as oxygen availability, redox potential, pH and others. To conclude, leaching tests can be used as important tools during landfill mining activities in order to bring valuable information not only for the design of treatment systems but also for an evaluation of the possibilities for recovery and beneficial use of the fine fraction.

Acknowledgments The authors would like to acknowledge the financial support from the Swedish Institute-SI and the Environmental Investment Centre in Estonia. We are grateful for the help obtained during the excavation and field work from the MSc and PhD students of Kaunas University of Technology (Department of Environmental Technology), Estonian University of Life Sciences (Institute of Agricultural and Environmental Sciences and the Department of Water Management), University of Latvia (Faculty of Chemistry), Taras Shevchenko National University of Kyiv and Linnaeus University (Environmental Science and Engineering Group). The fieldwork would not be done without crucial help of Olavi and Rein-Erik from RTS-Infra Ltd. Many thanks go to the support given by Valdo Liv and Mihkel Paljak.

References

1. Laner D, Crest M, Scharff H, Morris JWF, Barlaz MA (2012) A review of approaches for the long-term management of municipal solid waste landfills. Waste Manage 32:498–512
2. Masi S, Caniani D, Grieco E, Lioi DS, Mancini IM (2014) Assessment of the possible reuse of MSW coming from a landfill mining of old open dumpsites. Waste Manage 34:702–710
3. Xiaoli C, Shimaoka T, Xianyan C, Qiang G, Youcai Z (2007) Characteristics and mobility of heavy metals in an MSW landfill: implications in risk assessment and reclamation. J Hazard Mater 144:485–491
4. Hogland W (2002) Remediation of an old landfill site: soil analysis, leachate quality and gas production. Environ Sci Pollut R 1:49–54
5. Slack RJ, Gronow JR, Voulvoulis N (2005) Household hazardous waste in municipal landfills, contaminants in leachate. Sci Total Environ 337:119–137
6. Parodi A, Feuillade-Cathalifaud G, Pallier V, Mansour AA (2011) Optimization of municipal solid waste leaching test procedure: assessment of the part of hydrosoluble organic compounds. J Hazard Mater 186:991–998
7. Long Y-Y, Shen D-S, Wang H-T, Lu W-J, Zhao Y (2011) Heavy metal source analysis in municipal solid waste (MSW): case study on Cu and Zn. J Hazard Mater 186:1082–1087
8. Kaartinen T, Sormunen K, Rintala J (2013) Case study on sampling processing and characterization of landfilled municipal solid waste in the view of landfill mining. J Clean Prod 55:56–66
9. Krook J, Baas L (2013) Getting serious about mining the technosphere: a review of recent landfill mining and urban mining research. J Clean Prod 55:1–9
10. Hull RM, Krogmann U, Strom PF (2005) Composition and characteristics of excavated materials from a New Jersey landfill. J Environ Eng 3:478–490
11. Kurian J, Esakku S, Palanivelu K, Selvan A (2003) Studies on landfill mining at solid waste dumpsites in India. In: Procceedings Sardiniá03, Ninth International Landfill Symposium, Cagliari, Italy. pp 248–255
12. Mahmoudkhani M, Wilewska-Bien M, Steenari B-M, Theliander H (2008) Evaluating two test methods used for characterizing leaching properties. Waste Manage 28:133–141
13. International Organization of Standardization, 1990. ISO 8466/1. Water quality. Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1. Statistical evaluation of linear calibration function
14. Deutsches Institut für Normung e.V (1996). DIN 32645. Chemical analysis—decision limit, detection limit and determination limit—estimation in case of repeatability, terms, methods, evaluation
15. Deutsches Institut für Normung e.V (1986) DIN 38402-51. German standard methods for the examination of water, wastewater and sludge; general information (group A); calibration of analytical methods, evaluation of analytical results and linear calibration functions used to determine the performance characteristics of analytical methods (A51)
16. Kaczala F, Marques M, Vinrot E, Hogland W (2012) Stormwater run-off from an industrial log yard: characterization, contaminant correlation and first flush phenomenon. Environ Technol 33:1615–1628
17. Slomczyńska B, Slomczyński T (2004) Physico-chemical and toxicological characteristics of leachates from MSW Landfills. Pol J Environ Stud 13:627–637
18. Ziyang L, Youcai Z, Tao Y, Yu S, HuilI C, Nanwen Z, Renhua H (2009) Natural attrnuation and characterization of contaminants composition in landfill leachate under different disposing ages. Sci Total Environ 407:3385–3391

19. Cossu R, Lai T (2012) Washing of waste prior to landfilling. Waste Manage 32:869–878
20. Palleiro L, Rodríguez-Blanco ML, Taboada-Castro MM, Taboada-Castro MT (2013) The influence of discharge, pH, dissolved organic carbon, and suspended solids on the variability of concentration and partitioning of metals in a rural catchment. Water Air Soil Poll 224:1651. doi:10.1007/s11270-013-1651-9